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Office européen des brevets



(11) **EP 1 335 445 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
13.08.2003 Bulletin 2003/33

(51) Int Cl.7: **H01M 10/40**

(21) Application number: **01963395.7**

(86) International application number:
PCT/JP01/07434

(22) Date of filing: **29.08.2001**

(87) International publication number:
WO 02/031904 (18.04.2002 Gazette 2002/16)

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

(30) Priority: **12.10.2000 JP 2000311626**

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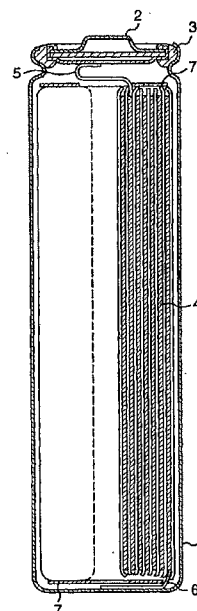
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(54) **ELECTROLYTE FOR NON-AQUEOUS CELL AND NON-AQUEOUS SECONDARY CELL**

(57) In a rechargeable non-aqueous electrolyte secondary battery using positive electrodes, negative electrodes and a non-aqueous electrolytic solution, additives to the electrolytic solution are used in combination, preferably in combination of at least two compounds selected from o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl, and thus there are provided batteries excellent in safety and storage characteristics.

FIG. 1



EP 1 335 445 A1

Description

TECHNICAL FIELD

5 [0001] The present invention relates to a non-aqueous electrolytic solution which can ensure safety of batteries at the time of overcharging with improving recovery characteristics of the batteries after storage at high temperatures, and to a non-aqueous type secondary battery using said electrolytic solution.

BACKGROUND ART

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[0002] Recently, AV devices and electronic devices such as personal computers of portable or cordless type have been rapidly developed, and secondary batteries which are small in size, light in weight and high in energy density are earnestly demanded as electric sources for driving these devices. Among them, non-aqueous electrolytic solution secondary batteries using a negative electrode containing lithium as an active material are hopefully expected as
15 batteries having high voltage and high energy density.

[0003] In the above batteries, lithium-containing metal oxides which show a voltage on the order of 4 V are used for positive electrode active materials, and materials capable of intercalation or deintercalation of lithium, such as carbonaceous materials, are used for negative electrodes.

[0004] One of the most important tasks in these non-aqueous electrolytic solution batteries is to ensure the safety.

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[0005] Particularly, in lithium ion secondary batteries, when they are charged in excess of a given charging voltage due to, for example, troubles of charging control circuits, they are in overcharged state, and lithium ions in the positive electrode are excessively extracted and migrate to negative electrode to cause absorption of lithium in an amount larger than the prescribed design capacity in the negative electrode or to cause precipitation of lithium as metallic lithium on the surface of negative electrode. If the batteries in such a state are further forcedly charged, internal resistance of the batteries increases and generation of heat due to the Joule's heat becomes great to cause abnormal heat
25 generation, and, in the worst case, to result in thermal runaway. By providing a current interrupting switch of temperature sensing type (for example, a positive temperature coefficient thermistor (PTC) or a temperature fuse) outside the batteries, the current is interrupted without fail, and safety can be ensured at the time of generation of abnormal heat. Furthermore, in order to solve the problem of overcharge, a means of interrupting the charging current upon sensing the change of internal pressure of batteries is generally employed as disclosed in U.S. Patent No.4943497.

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[0006] However, in the case of using such a mechanical current interrupting mechanism, reduction of cost is difficult and, furthermore, with the batteries becoming smaller and thinner, it becomes structurally difficult to insert the mechanism in the batteries.

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[0007] For solving the above problems, there is proposed a method of adding to the electrolytic solution an additive which causes a reversible redox reaction, thereby to self-consume the electric energy introduced into the batteries as a redox shuttle (for example, JP-A-1-206571, JP-A-6-338347, JP-A-7-302614, etc.).

[0008] However, in the method of using the redox shuttle, when the overcharging current becomes great, there are limits in charge transfer reaction rate and lithium ion transfer rate, and, thus, it cannot be said that the method provides a sufficient safety.

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[0009] For solving the above problems, JP-9-50822, JP-A-10-50342, JP-9-106835, JP-10-321258, Japanese Patent No. 2939469, and JP-A-2000-58117 propose a means of adding to batteries an aromatic compound having a methoxy group and a halogen group, biphenyl or thiophene, or an aromatic ether compound, which polymerizes at the time of overcharging to result in rising of temperature and, thus, to ensure the safety.

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DISCLOSURE OF INVENTION

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[0010] In the case of the batteries in which a current interrupting switch of temperature sensing type (for example, a positive temperature coefficient thermistor (PTC) or a temperature fuse) is provided outside the batteries against abnormal heat generation, when an excessively large overcharging current (5-6 C) of more than 5-6 times the rated capacity passes, the device per se generates heat due to the current and resistance increases, thereby interrupting the current, and thus the safety can be ensured, but in the case of a current generally used for charging and discharging the batteries (less than 1-2 C at the maximum), the rising of temperature is insufficient and the resistance does not increase. When overcharging is carried out at such a current value, the safety cannot be sufficiently ensured. If the setting is made so that the resistance increases in the generally used current region, naturally the inherent performance
55 of the batteries are damaged.

[0011] In the case of adding to the batteries the above-mentioned additives such as aromatic compound having a methoxy group and a halogen group, biphenyl or thiophene, and an aromatic ether compound, it has been confirmed that in the generally used current ranges, the additives polymerize on the electrodes in overcharged state, and the

safety is improved.

[0012] However, it has been found that these additives must be added in an amount of not less than 1% by weight for ensuring the safety at the time of overcharging, but if the additives are added in a large amount, in an shelf life test, for example, an environment test (80°C) which supposes the case of leaving them in a car in summer, these additives

partially react to cover the active material, resulting in considerable deterioration of the battery characteristics. [0013] The above phenomenon is considered to occur because oxidative polymerization potential of the additives lowers due to exposure of the battery to a high temperature environment, and, furthermore, the potential distribution in the charged electrode is not uniform and higher potential portions are partially present, and, as a result, the additives react even in the ordinary environment of potential at which battery is used.

[0014] The above problem of deterioration due to storage can be solved, for example, by using an additive high in oxidative polymerization starting potential (for example, cyclohexylbenzene), but in this case, since the reaction potential of the additive is rather high at the time of the overcharging, the safety of overcharging cannot sufficiently be ensured.

[0015] The present invention solves the above problems and to provide a battery excellent in high-temperature storage characteristics while ensuring the safety at overcharging.

[0016] In order to solve the above problems, according to the present invention, in a non-aqueous electrolytic solution in which an electrolyte is dissolved in a non-aqueous solvent, two or more organic compounds differing in oxidative polymerization reaction potential are added. Preferably, organic compounds of relatively low oxidation reaction potential are added in a very small amount, preferably not less than 0.01% by weight and less than 1.0% by weight based on the total amount of the electrolytic solution, thereby to control the recovery characteristics after storage and the safety during overcharging. Specifically, it is preferred to add at least two organic compounds selected from o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl.

[0017] It is preferred that not less than 1.0% by weight and not more than 3.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of triphenylene are contained in the non-aqueous solvent.

[0018] Furthermore, it is preferred that not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of biphenyl are contained in the non-aqueous solvent.

[0019] Moreover, it is preferred that not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl are contained in the non-aqueous solvent.

[0020] Further, it is preferred that not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene, not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of biphenyl are contained in the non-aqueous solvent.

[0021] Furthermore, it is preferred that all of o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained in the non-aqueous solvent and the total amount of them is 0.4-5% by weight based on the non-aqueous solvent.

[0022] These organic compounds are particularly effective when the positive electrodes comprise a material containing a lithium-containing metal oxide and the negative electrodes comprise a material containing graphite, and the non-aqueous electrolytic solution exerts the higher effect when it is an electrolytic solution in which a lithium salt as a solute is dissolved in a non-aqueous solvent mainly composed of a cyclic carbonate and a chain carbonate.

[0023] The cyclic carbonate is preferably at least one compound selected from ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC) and vinylene carbonate (VC).

[0024] The chain carbonate is preferably at least one compound selected from dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC) and ethylpropyl carbonate (EPC).

BRIEF DESCRIPTION OF DRAWING

[0025]

FIG. 1 is a longitudinal sectional view of a cylindrical battery in the examples of the present invention and in the comparative examples.

BEST MODE FOR CARRYING OUT THE INVENTION

[0026] In the present invention, recovery characteristics after storage and safety during overcharging can be controlled by adding two or more organic compounds differing in oxidative polymerization reaction potential to the electrolytic solution.

[0027] Examples of organic compounds differing in oxidative polymerization potential contained in the electrolytic solution for non-aqueous type batteries in which an electrolyte is dissolved in a non-aqueous solvent are o-terphenyl,

triphenylene, cyclohexylbenzene and biphenyl. As to the content of the organic compounds, the weight of the organic compound of relatively higher oxidative polymerization potential is preferably not less than 1.0% by weight and not more than 5.0% by weight based on the total amount of the non-aqueous electrolytic solution. The weight of the organic compound of relatively lower oxidative polymerization potential is preferably not less than 0.01% by weight and less than 1.0% by weight based on the total amount of the non-aqueous electrolytic solution. Furthermore, the weight ratio of the organic compound of relatively higher oxidative polymerization reaction potential and the organic compound of relatively lower oxidative polymerization reaction potential is preferably not lower than 20:1 and not higher than 2:1, more preferably not lower than 10:1 and not higher than 4:1.

[0028] In order to improve the recovery characteristics after storage, the amount of the organic compound of relatively lower oxidative polymerization starting potential (for example, biphenyl) is preferably smaller, but in order to ensure the safety at overcharging, the organic compound must react as much as possible at overcharging, namely, the amount is preferably rather larger.

[0029] According to the present invention, two or more organic compounds differing in oxidative polymerization reaction potential (hereinafter sometimes referred to as "additives") are used, and the amount of the organic compound of relatively lower oxidative polymerization starting potential (for example, biphenyl) is conspicuously reduced in this system, thereby maintaining excellent storage characteristics, and on the other hand the organic compounds react only slightly at the overcharging, whereby polarization at the overcharging increases, and the organic compound of relatively higher oxidative polymerization starting potential (for example, cyclohexylbenzene) react at an early stage, and thus the safety can be ensured. As a result, there can be attained both the recovery properties after storage and the insurance of safety at overcharging, which cannot be attained with addition of each organic compound singly.

[0030] Since the additives in the present invention do not aim at an action as redox shuttles, the oxidation reaction is desirably irreversible and they differ in purpose from JP-A-7-302614 and JP-A-9-50822 which aim at reversibility of redox reaction.

[0031] As the lithium-containing composite oxides used as positive electrode active materials in the present invention, mention may be made of, for example, Li_xCoO_z , Li_xNiO_z (U.S. Patent No.4302518), Li_xMnO_z , $\text{Li}_x\text{CO}_y\text{Ni}_{1-y}\text{O}_z$ (JP-A-63-299056), $\text{Li}_x\text{CoV}_{1-x}\text{O}_z$, $\text{Li}_x\text{Ni}_{1-y}\text{M}_y\text{O}_z$ ($\text{M} = \text{Ti, V, Mn, Fe}$), $\text{Li}_x\text{Co}_a\text{Ni}_b\text{M}_c\text{O}_z$ ($\text{M} = \text{Ti, Mn, Al, Mg, Fe, Zr}$), $\text{Li}_x\text{Mn}_2\text{O}_4$, $\text{Li}_x\text{Mn}_{2(1-y)}\text{M}_{2y}\text{O}_4$ ($\text{M} = \text{Na, Mg, Sc, Y, Fe, Co, Ni, Ti, Zr, Cu, Zn, Al, Pb, Sb}$) ($x=0-1.2$, $y=0-1.0$, $f=0.9-0.98$, $z=1.9-2.3$, $a+b+c=1.0$, $0 \leq a \leq 1$, $0 \leq b \leq 1$, $0 \leq c < 1$). The value x is a value before starting of charging and discharging, which increases or decreases by charging and discharging.

[0032] The lithium-containing composite oxides used as positive electrode active materials in the present invention can be prepared by mixing carbonate, nitrate, oxide or hydroxide of lithium with carbonate, nitrate, oxide or hydroxide of a transition metal such as cobalt, manganese or nickel at a desired composition, grinding the mixture and firing the powder or by a solution reaction. The firing method is especially preferred, and the firing temperature can be 250-1500°C at which a part of the mixed compound is decomposed and molten. The firing time is preferably 1-80 hours. The firing gas atmosphere can be any of air atmosphere, oxidizing atmosphere or reducing atmosphere, and has no special limitation.

[0033] In the present invention, a plurality of different positive electrode active materials may be used in combination.

[0034] As current collectors of positive electrodes, there may be used any electron conductors as long as they do not undergo chemical changes in the constructed batteries. For examples, as materials of the current collectors, there may be used stainless steel, aluminum, titanium and carbon, and aluminum or aluminum alloys are especially preferred. As for the shape of the current collectors, they may be in the form of foil, film, sheet, net, punched material, lath, porous material, foamed material, fiber group, shaped nonwoven fabric, and the like. The surface of the current collectors may be made rough by a surface treatment. Thickness thereof is not particularly limited, and those of 1-500 μm are used.

[0035] The negative electrode materials used in the present invention may be lithium alloys, alloys, intermetallic compounds, carbons, organic compounds, inorganic compounds, metal complexes and organic high molecular compounds, which are capable of absorbing and releasing lithium ions. These may be used each alone or in combination.

[0036] As the carbonaceous materials, mention may be made of, for example, cokes, pyrolytic carbons, natural graphite, artificial graphite, mesocarbon microbeads, graphitized mesophase spherules, vapor deposited carbons, glassy carbons, carbon fibers (polyacrylonitrile fibers, pitch fibers, cellulose fibers and vapor deposited carbon fibers), amorphous carbons, and carbons prepared by firing organic materials. These may be used each alone or in combination. Among them, preferred are graphite materials such as those obtained by graphitizing mesophase spherules, natural graphite and artificial graphite. These negative electrode materials may be used as composites, and, for example, combinations of carbon with alloys, carbon with inorganic compounds, and the like can be considered.

[0037] In the present invention, since Li is contained in the positive electrode active material, negative electrode materials which do not contain Li (such as carbon) can be used. Moreover, when Li is added to such negative electrode materials which do not contain Li in a small amount (about 0.01-10 parts by weight based on 100 parts by weight of the negative electrode materials), even if the materials become inactive owing to the reaction of a part of Li with electrolyte, Li can be supplemented with Li contained in the negative electrode materials, which is preferred. Li can be

contained in the negative electrode materials, for example, in the following manner. That is, lithium metal which is molten by heating is coated on a current collector to which a negative electrode material is pressed, thereby impregnating the negative electrode material with Li, or lithium metal is previously applied to electrode group by press bonding and Li is electrochemically doped in the negative electrode material in the electrolytic solution.

[0038] As current collectors of negative electrodes, there may be used any electron conductors as long as they do not undergo chemical changes in the constructed batteries. For example, as materials of the collectors, there may be used stainless steel, nickel, copper, titanium, etc. Copper or copper alloys are especially preferred.

[0039] As for the shape of the current collectors, they may be in the form of foil, film, sheet, net, punched material, lath, porous material, foamed material, fiber group, shaped nonwoven fabric, and the like. Moreover, the surface of the current collectors may be made rough by a surface treatment. Thickness is not particularly limited, and those of 1-500 μm are used.

[0040] The non-aqueous electrolytic solution in the present invention comprises a solvent and a lithium salt dissolved in the solvent. As the non-aqueous solvents, mention may be made of cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC) and vinylene carbonate (VC), non-cyclic carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC), ethylpropyl carbonate (EPC), methylpropyl carbonate (MPC), methylisopropyl carbonate (MIPC) and dipropyl carbonate (DPC), aliphatic carboxylic acid esters such as methyl formate, methyl acetate, methyl propionate and ethyl propionate, γ -lactones such as γ -butyrolactone, non-cyclic ethers such as 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE) and ethoxymethoxyethane (EME), cyclic ethers such as tetrahydrofuran and 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolan, alkyl phosphate esters such as trimethyl phosphate, triethyl phosphate and trioctyl phosphate, and fluorides of them. These may be used each alone or in admixture of two or more. Among them, it is preferred to use a mixed system of a cyclic carbonate and a non-cyclic carbonate or a mixed system of a cyclic carbonate, non-cyclic carbonate and an aliphatic carboxylic acid ester as a main component.

[0041] The lithium salts which are dissolved in these solvents include, for example, LiClO_4 , LiBF_4 , LiPF_6 , LiAlCl_4 , LiSbF_6 , LiSCN , LiCl , LiCF_3SO_3 , LiCF_3CO_2 , LiAsF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ (JP-A-57-74974), $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiPF}_3(\text{CF}_3)_3$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$, etc. These may be contained each alone or in combination of two or more in the electrolytic solution, etc. Among them, it is especially preferred that the solution contains LiPF_6 .

[0042] Especially preferable non-aqueous electrolytic solution in the present invention is one which contains at least ethylene carbonate and ethylmethyl carbonate and LiPF_6 as a lithium salt. The amount of the electrolytic solution contained in the battery is not particularly limited, and it can be used in a necessary amount depending on the amount of positive electrode active material and that of negative electrode material and the size of the battery. The amount of the lithium salt dissolved in the non-aqueous solvent is not particularly limited, but is preferably 0.2-2 mol/l, especially preferably 0.5-1.5 mol/l.

[0043] The electrolytic solution is ordinarily used by impregnating or filling a separator such as of porous polymer or nonwoven fabric with the electrolytic solution.

[0044] Moreover, there may be used a gelled electrolyte comprising an organic solid electrolyte containing the non-aqueous electrolytic solution. As the organic solid electrolyte, polymeric matrix materials such as polyethylene oxide, polypropylene oxide, polyvinylidene fluoride and derivatives, mixtures and composites of these materials are effective. Especially preferred are copolymers of vinylidene fluoride and hexafluoropropylene and mixtures of polyvinylidene fluoride and polyethylene oxide.

[0045] As the separator, an insulating microporous thin film having a high ion permeability and a desired mechanical strength is used. The separator preferably has a function of closing the pores at a temperature of 80°C or higher to enhance the resistance. Sheets or nonwoven fabrics made from olefin polymers comprising one or combination of polypropylene and polyethylene or glass fibers are used from the points of organic solvent resistance and hydrophobic properties. Pore diameter of the separator is preferably in such a range that active materials, binders and conducting agents which are released from the electrode sheets do not permeate through the pores, and, for example, the pore diameter is preferably 0.01-1 μm . The thickness of the separator is generally 5-300 μm . The porosity is determined depending on the permeability to electron or ion, kind of materials or film thickness, and is desirably 30-80%.

[0046] The shape of batteries can be any of sheet type, cylinder type, flat type, rectangular type, etc. When the shape of batteries is sheet type, cylinder type or rectangular type, the mix of positive electrode active material or negative electrode material is used mainly by coating on a current collector, then drying and compressing the collector.

[0047] The shape of the rolled electrodes in the present invention is not necessarily in the form of true cylinder, and may be in the form of ellipsoidal cylinder having a ellipsoidal section or in the form of square pillar such as rectangle.

[0048] Preferred combinations in the present invention are combinations of the preferred chemical materials and the preferred battery constituting parts mentioned above. Especially preferred are those which contain Li_xCoO_2 , Li_xNiO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 \leq x \leq 1$) as positive electrode active materials, and acetylene black as a conducting agent. The current collector of positive electrode is made of stainless steel or aluminum, and is in the form of net, sheet, foil or lath. The negative electrode material preferably contains at least one compound such as alloy and carbonaceous material. The

current collector of negative electrode is made of stainless steel or copper and is in the form of net, sheet, foil or lath. Carbon materials such as acetylene black and graphite as the electron conducting agent may be contained in the mix used together with positive electrode active materials or negative electrode materials. As the binders, there may be used fluorine-containing thermoplastic compounds such as polyvinylidene fluoride and polytetrafluoroethylene, polymers containing acrylic acid, and elastomers such as styrene-butadiene rubber and ethylene-propylene terpolymer each alone or in admixture. The electrolytic solution preferably contains cyclic or non-cyclic carbonates such as ethylene carbonate, diethyl carbonate, dimethyl carbonate and ethylmethyl carbonate or additionally aliphatic carboxylic acid esters such as methyl acetate and methyl propionate, and LiPF_6 as a lithium salt. The separator preferably comprises polypropylene or polyethylene each alone or in combination. The battery may have any shapes such as cylindrical shape, flat shape, and rectangular shape. The battery preferably has a means for ensuring safety against errors in working (e.g., an internal pressure releasing type safety valve, a separator which enhances resistance at high temperatures).

EXAMPLES

[0049] Examples of the present invention will be explained below referring to the drawing.

Example 1

[0050] FIG. 1 is a longitudinal sectional view of the cylindrical battery used in this example. In FIG. 1, the reference numeral 1 indicates a battery case made by working a stainless steel plate having resistance to organic electrolytic solution, 2 indicates a sealing plate provided with a safety valve, 3 indicates an insulation packing, 4 indicates an electrode plate group, and positive electrode and negative electrode with separator interposed between the positive electrode and the negative electrode are rolled a plurality of times into a spiral form and inserted in the case 1. A positive electrode lead 5 is drawn from the positive electrode and connected to the sealing plate 2, and a negative electrode lead 6 is drawn from the negative electrode and connected to the bottom of the battery case 1. The reference numeral 7 indicates an insulation ring, which is provided at the upper and lower portions of the electrode plate group 4. The positive electrode, the negative electrode, and others will be explained in detail below.

[0051] The positive electrode was made in the following manner. Li_2CO_3 and Co_3O_4 were mixed and fired at 900°C for 10 hours to prepare an LiCoO_2 powder. This powder was mixed with 3% of acetylene black and 7% of a fluorocarbon polymer binder based on the weight of the LiCoO_2 powder, followed by suspending the mixture in an aqueous carboxymethyl cellulose solution to prepare a positive electrode mix paste. The resulting positive electrode mix paste was coated on the surface of an aluminum foil of 20 μm in thickness which was a positive electrode current collector, and the coat was dried, followed by rolling to make a positive electrode plate of 0.18 mm in thickness, 37 mm in width and 390 mm in length.

[0052] For the negative electrode, a mesophase spherule which was graphitized at a high temperature of 2800°C (hereinafter referred to as "mesophase graphite") was used. This mesophase graphite was mixed with 3% of a styrene-butadiene rubber based on the weight of the mesophase graphite, and then the mixture was suspended in an aqueous carboxymethyl cellulose solution to prepare a paste. This negative electrode mix paste was coated on both sides of a Cu foil of 0.02 mm in thickness and dried, followed by rolling to make a negative electrode plate of 0.20 mm in thickness, 39 mm in width and 420 mm in length.

[0053] A lead made of aluminum was attached to the positive electrode plate and a lead made of nickel was attached to the negative electrode plate, and the positive electrode plate and the negative electrode plate with a polyethylene separator of 0.018 mm in thickness, 45 mm in width and 840 mm in length interposed between the positive electrode plate and the negative electrode plate were rolled into a spiral form and inserted in a battery case of 17.0 mm in diameter and 50.0 mm in height. The electrolytic solution used was prepared by dissolving 1 mol/liter of LiPF_6 in a mixed solvent comprising EC and EMC at a volume ratio of 30:70, and as additives, 2% by weight of o-terphenyl and 0.2% by weight of triphenylene based on the total amount of the electrolytic solution were added to the electrolytic solution. The electrolytic solution was poured into the battery case, and then the case was sealed to make a battery 1 (battery capacity: 800 mAh) of the present invention.

Example 2

[0054] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that cyclohexylbenzene in an amount of 2% by weight and biphenyl in an amount of 0.2% by weight based on the total amount of the electrolytic solution were used as the additives to the electrolytic solution. The thus obtained battery was referred to as battery 2 of the present invention.

Example 3

[0055] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that cyclohexylbenzene in an amount of 2% by weight and o-terphenyl in an amount of 0.2% by weight based on the total amount of the electrolytic solution were used as the additives to the electrolytic solution. The thus obtained battery was referred to as battery 3 of the present invention.

Example 4

[0056] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that cyclohexylbenzene in an amount of 2% by weight, biphenyl in an amount of 0.2% by weight and o-terphenyl in an amount of 0.2% by weight based on the total amount of the electrolytic solution were used as the additives to the electrolytic solution. The thus obtained battery was referred to as battery 4 of the present invention.

Example 5

[0057] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that cyclohexylbenzene in an amount of 2% by weight, biphenyl in an amount of 0.2% by weight, o-terphenyl in an amount of 0.2% by weight and triphenylene in an amount of 0.1% by weight based on the total amount of the electrolytic solution were used as the additives to the electrolytic solution. The thus obtained battery was referred to as battery 5 of the present invention.

Comparative Example 1

[0058] A cylindrical battery was made in the same manner as in Example 1, except that the additives to the electrolytic solution were not used. The thus obtained battery was referred to as a comparative battery (battery 6).

Comparative Example 2

[0059] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that biphenyl was used in an amount of 2.0% by weight based on the total amount of the electrolytic solution as the additive to the electrolytic solution. The thus obtained battery was referred to as a comparative battery (battery 7).

Comparative Example 3

[0060] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that cyclohexylbenzene was used in an amount of 2.0% by weight based on the total amount of the electrolytic solution as the additive to the electrolytic solution. The thus obtained battery was referred to as a comparative battery (battery 8).

Comparative Example 4

[0061] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that o-terphenyl was used in an amount of 2.0% by weight based on the total amount of the electrolytic solution as the additive to the electrolytic solution. The thus obtained battery was referred to as a comparative battery (battery 9).

Comparative Example 5

[0062] A cylindrical battery of spiral type was made in the same manner as in Example 1, except that biphenyl was used in an amount of 0.2% by weight based on the total amount of the electrolytic solution as the additive to the electrolytic solution. The thus obtained battery was referred to as a comparative battery (battery 10).

[0063] Then, as overcharging tests, 20 cells each of the batteries 1-5 of the present invention and the comparative batteries 6-9 were subjected to overcharging at 0.8 A (1C) from charged state at an environmental temperature of 20°C, and it was examined whether abnormal heat generation occurred or not in the batteries. The number of cells among 20 cells in which abnormal heat generation occurred is shown in Tables 1 and 2.

[0064] Furthermore, as high-temperature storage tests, the batteries in charged state were left to stand at 80°C for 4 days, and the discharge capacity at 1C was compared with the discharge capacity before storing, and capacity recovery rate after storing was calculated. (Capacity recovery rate after storing = (1C discharge capacity after storing) / (1C discharge capacity before storing) X 100(%)).

Table 1

(Example)			
No.	Additives	Occurrence of abnormal heat generation	Recovery rate after storage (%)
1	o-Terphenyl (2%) + triphenylene (0.2%)	0/20	75
2	Cyclohexylbenzene (2%) + biphenyl (0.2%)	0/20	85
3	Cyclohexylbenzene (2%) + o-terphenyl (0.2%)	2/20	82
4	Cyclohexylbenzene (2%) + biphenyl (0.2%) + o-terphenyl (0.2%)	0/20	84
5	Cyclohexylbenzene (2%) + biphenyl (0.2%) + o-terphenyl (0.2%) + triphenylene (0.1%)	0/20	83

Table 2

(Comparative Example)			
No.	Additives	Occurrence of abnormal heat generation	Recovery rate after storage (%)
6	No	20/20	87
7	Biphenyl (2%)	0/20	17
8	Cyclohexylbenzene (2%)	13/20	85
9	o-Terphenyl (2%)	7/20	69
10	Biphenyl (0.2)	14/20	82

[0065] As shown in Table 2, in the battery 6 having no additives, the phenomenon of abnormal heat generation occurred in all of 20 cells when they were subjected to overcharging. Hitherto, the safety of batteries has been ensured by providing a plurality of safety mechanisms comprising a protective circuit for charging voltage and a current interrupting mechanism, but the abnormal heat generation may occur in case no safety protection was provided as in the Comparative Example 1.

[0066] It can be seen that in the battery 7 of Comparative Example 2 in which biphenyl was added as the additive, abnormal heat generation did not occur even when it was subjected to overcharging, and safety could be ensured, but the recovery rate after storing at high temperatures was very low, namely, 17%.

[0067] This battery was disassembled after storing and analyzed to find a film which was considered to be a polymerization product was formed on the surface of the positive electrode, and it was presumed that the recovery rate decreased due to the hindrance to charging and discharging reaction of lithium ion.

[0068] Furthermore, in the battery 8 of Comparative Example 3 in which only cyclohexylbenzene high in reaction starting potential was contained, the recovery rate after storing at high temperatures was high, namely, 85%, and this battery showed characteristics substantially equal to those of the battery 6 containing no additives, but was insufficient in safety at the time of overcharging and more than half of the cells resulted in abnormal heat generation.

[0069] In the case of addition of o-terphenyl which was relatively high in reaction starting potential, ignition rate at overcharging somewhat decreased, but the decrease was still insufficient and, further, the recovery rate after storing was also insufficient.

[0070] When the amount of biphenyl of low reaction starting potential was reduced, the recovery rate after storing increased, but safety at overcharging could not be ensured as in the battery 10 of Comparative Example 5.

[0071] As explained above, it is not easy to ensure both the safety at overcharging and the high-temperature storage characteristics by using a single additive.

[0072] In comparison with the batteries of the comparative examples, in the batteries such as batteries 1-5 of the

present invention in which two or more additives were contained, by adding a small amount of an additive of relatively lower reaction starting potential (biphenyl, o-terphenyl, triphenylene) in each system, the recovery rate after storing was improved and a recovery rate of more than 70% was maintained, and, moreover, since the additive of lower reaction starting potential which slightly reacted during the overcharging increased the polarization at overcharging, the additive of higher reaction starting potential started the reaction at the early stage to enhance the safety at overcharging. Thus, batteries superior in recovery characteristics in storing and high in safety at overcharging could be realized.

[0073] From the point of maintaining the safety at overcharging, the amount of cyclohexylbenzene is preferably not less than 1.0% by weight and not more than 5.0% by weight.

[0074] Furthermore, from the point of maintaining the recovery characteristics in storing, the amount of biphenyl or triphenylene is preferably not less than 0.01% by weight and less than 1.0% by weight.

INDUSTRIAL APPLICABILITY

[0075] As explained above, the present invention can provide batteries having high safety against overcharging and excellent in recovery characteristics in storing at high temperatures by combining additives to electrolytic solutions.

[0076] Portable telephones, portable information terminal devices, cam coders, personal computers, PDA, portable audio devices, electric cars, electric sources for road leveling, and the like which are high in safety can be provided by using the non-aqueous type electrolyte secondary batteries as mentioned above.

Claims

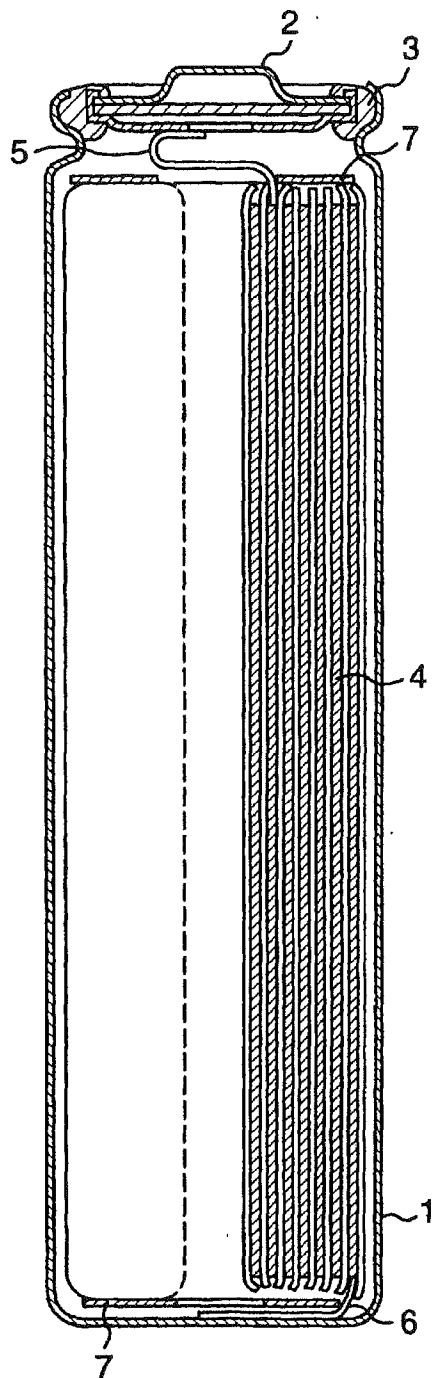
1. A non-aqueous electrolytic solution for non-aqueous type batteries in which an electrolyte is dissolved in a non-aqueous solvent, **characterized by** containing two or more organic compounds differing in oxidative polymerization potential, with a proviso that weight of the organic compound of relatively lower oxidative polymerization potential is less than that of the organic compound of relatively higher oxidative polymerization potential.
2. An electrolytic solution for non-aqueous type batteries according to claim 1, wherein two or more organic compounds selected from o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained as the organic compounds differing in oxidative polymerization potential.
3. An electrolytic solution for non-aqueous type batteries according to claim 1, wherein not less than 1.0% by weight and not more than 3.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of triphenylene based on the total amount of the non-aqueous electrolytic solution are contained.
4. An electrolytic solution for non-aqueous type batteries according to claim 1, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
5. An electrolytic solution for non-aqueous type batteries according to claim 1, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
6. An electrolytic solution for non-aqueous type batteries according to claim 1, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene, not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
7. An electrolytic solution for non-aqueous type batteries according to claim 1, wherein all of o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained and the total amount of them is 0.4-5% by weight based on the total amount of the non-aqueous electrolytic solution.
8. An electrolytic solution for non-aqueous type batteries having a positive electrode comprising a material containing a lithium-containing metal oxide as a positive electrode active material and a negative electrode comprising a material containing graphite as a negative electrode active material, **characterized in that** the non-aqueous electrolytic solution contains a non-aqueous solvent mainly composed of a cyclic carbonate and a chain carbonate in which a lithium salt is dissolved as a solute, and further contains two or more organic compounds differing in oxidative polymerization potential, with a proviso that weight of the organic compound of relatively lower oxidative

polymerization potential is less than that of the organic compound of relatively higher oxidative polymerization potential.

- 5 9. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein two or more organic compounds selected from o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained as the organic compounds differing in oxidative polymerization potential.
- 10 10. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein not less than 1.0% by weight and not more than 3.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of triphenylene based on the total amount of the non-aqueous electrolytic solution are contained.
- 15 11. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
- 20 12. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
- 25 13. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene, not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
- 30 14. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein all of o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained and the total amount of them is 0.4-5% by weight based on the total amount of the non-aqueous electrolytic solution.
- 35 15. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein the cyclic carbonate is at least one compound selected from ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC) and vinylene carbonate (VC).
- 40 16. An electrolytic solution for non-aqueous type batteries according to claim 8, wherein the chain carbonate is at least one compound selected from dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC) and ethylpropyl carbonate (EPC).
- 45 17. A non-aqueous type secondary battery containing a non-aqueous electrolytic solution in which an electrolyte is dissolved in a non-aqueous solvent, **characterized in that** two or more organic compounds differing in oxidative polymerization potential are further contained in the non-aqueous electrolytic solution, with a proviso that weight of the organic compound of relatively lower oxidative polymerization potential is less than that of the organic compound of relatively higher oxidative polymerization potential.
- 50 18. A non-aqueous type secondary battery according to claim 17, wherein two or more organic compounds selected from o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained as the organic compounds differing in oxidative polymerization potential.
- 55 19. A non-aqueous type secondary battery according to claim 17, wherein not less than 1.0% by weight and not more than 3.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of triphenylene based on the total amount of the non-aqueous electrolytic solution are contained.
20. A non-aqueous type secondary battery according to claim 17, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
21. A non-aqueous type secondary battery according to claim 17, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl based on the total amount of the non-aqueous electrolytic solution are contained.

22. A non-aqueous type secondary battery according to claim 17, wherein all of not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene, not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
23. A non-aqueous type secondary battery according to claim 17, wherein all of o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained and the total amount of them is 0.4-5% by weight based on the total amount of the non-aqueous electrolytic solution.
24. A non-aqueous type secondary battery having a positive electrode comprising a material containing a lithium-containing metal oxide as a positive electrode active material, a negative electrode comprising a material containing graphite as a negative electrode active material and a non-aqueous electrolytic solution, **characterized in that** the non-aqueous electrolytic solution contains a non-aqueous solvent mainly composed of a cyclic carbonate and a chain carbonate in which a lithium salt is dissolved as a solute, and further contains two or more organic compounds differing in oxidative polymerization potential, with a proviso that weight of the organic compound of relatively lower oxidative polymerization potential is less than that of the organic compound of relatively higher oxidative polymerization potential.
25. A non-aqueous type secondary battery according to claim 24, wherein two or more organic compounds selected from o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained as the organic compounds differing in oxidative polymerization potential.
26. A non-aqueous type secondary battery according to claim 24, wherein not less than 1.0% by weight and not more than 3.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of triphenylene based on the total amount of the non-aqueous electrolytic solution are contained.
27. A non-aqueous type secondary battery according to claim 24, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
28. A non-aqueous type secondary battery according to claim 24, wherein not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene and not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
29. A non-aqueous type secondary battery according to claim 24, wherein all of not less than 1.0% by weight and not more than 5.0% by weight of cyclohexylbenzene, not less than 0.01% by weight and less than 1.0% by weight of o-terphenyl and not less than 0.01% by weight and less than 1.0% by weight of biphenyl based on the total amount of the non-aqueous electrolytic solution are contained.
30. A non-aqueous type secondary battery according to claim 24, wherein all of o-terphenyl, triphenylene, cyclohexylbenzene and biphenyl are contained and the total amount of them is 0.4-5% by weight based on the total amount of the non-aqueous electrolytic solution.
31. A non-aqueous type secondary battery according to claim 24, wherein the cyclic carbonate is at least one compound selected from ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC) and vinylene carbonate (VC).
32. A non-aqueous type secondary battery according to claim 24, wherein the chain carbonate is at least one compound selected from dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC) and ethylpropyl carbonate (EPC).

FIG. 1



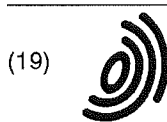
INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/07434

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ H01M 10/40		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ H01M 10/40, 6/00-6/22		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	JP 2001-126765 A (GS-Melcotec Co., Ltd.), 11 May, 2001 (11.05.01), Par. Nos. [0007] to [0010], [0018], [0025] to [0034] (Family: none)	1, 8 15-17 24, 31 32 2-7 9-14 18-23 25-30
PA		
A	JP 2000-58116 A (Sanyo Electric Co., Ltd.), 25 February, 2000 (25.02.00), Full text (Family: none)	1-32
A	US 5879834 A (NEC Moil Energy Ltd.), 09 March, 1999 (09.03.99), Full text & JP 9-106835 A	1-32
PA	JP 2001-210364 A (Mitsubishi Chemical Corporation), 03 August, 2001 (03.08.01), Full text (Family: none)	1-32
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Date of the actual completion of the international search 27 November, 2001 (27.11.01)		Date of mailing of the international search report 11 December, 2001 (11.12.01)
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Form PCT/ISA/210 (second sheet) (July 1992)



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European Patent Office
Office européen des brevets



(11) **EP 1 361 622 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
12.11.2003 Bulletin 2003/46

(21) Application number: **02716365.8**

(22) Date of filing: **24.01.2002**

(51) Int Cl.7: **H01M 10/40**

(86) International application number:
PCT/JP02/00518

(87) International publication number:
WO 02/059999 (01.08.2002 Gazette 2002/31)

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **24.01.2001 JP 2001015466**
24.01.2001 JP 2001015467

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(54) **NONAQUEOUS ELECTROLYTIC SOLUTION AND LITHIUM SECONDARY BATTERIES**

(57) In order to manufacture a lithium secondary battery having excellent performances in safety under overcharge condition, cycle property, electric capacity, and storage endurance, 0.1 wt.% to 10 wt.% of a tert-alkylbenzene compound is favorably incorporated into

a non-aqueous electrolytic solution comprising a non-aqueous solvent and an electrolyte, preferably in combination with 0.1 wt.% to 1-5 wt.% of a biphenyl compound.

EP 1 361 622 A1

Description

[Field of Invention]

- 5 [0001] The present invention relates to a lithium secondary battery showing high safety under the condition of overcharge, and excellent battery characteristics in cycle property, electric capacity and storage endurance, and further relates to a non-aqueous electrolytic solution favorably employable for preparing the lithium secondary battery.

[Background of Invention]

10

- [0002] Recently, lithium secondary batteries are generally employed as electric sources for driving small electronic devices. They are also employed as electric sources for driving portable electronic transmission apparatuses such as small size video cameras, cellular phones, and note-size personal computers. They are also expected as electric sources for motor cars. The lithium secondary battery essentially comprises a positive electrode, a non-aqueous electrolytic solution, and a negative electrode. A lithium secondary battery utilizing a positive electrode of lithium compound oxide such as LiCoO_2 and a negative electrode of carbonaceous material or lithium metal is preferably used. As a non-aqueous solvent of the electrolytic solution for lithium secondary batteries, a carbonate such as ethylene carbonate (EC) or propylene carbonate (PC) is preferably used.

15

- [0003] In the lithium secondary battery, the positive electrode releases an excessive lithium and the excessive lithium deposits on the negative electrode to produce dendrite, if the battery is overcharged to exceed the ordinary working voltage. Therefore, both of the positive and negative electrodes become unstable. When both electrodes become unstable, the carbonate in the electrolytic solution decomposes upon contact with the unstable electrodes and an exothermic reaction rapidly occurs. Accordingly, the battery abnormally generates heat and safety of the battery lowers. This phenomenon makes increased troubles in the case that the battery generates an electric current of an increased energy density.

25

[0004] Until now, it has been proposed that an addition of a small amount of an aromatic compound to the electrolytic solution is effective to assure the safety under the overcharge condition.

- [0005] JP-A-7-302614 describes that an organic compound having a molecular weight of 500 or less and a π -electron orbit which gives a reversible oxidation-reduction potential at a potential of noble side relative to the positive electrode potential under the fully charged condition, which is represented by an anisole derivative, is used as an additive for an electrolytic solution.

30

- [0006] JP-A-2000-156243 describes that an organic compound having a π -electron orbit which gives a reversible oxidation-reduction potential at a potential of noble side relative to the positive electrode potential under the fully charged condition, which is represented by an anisole derivative, biphenyl, and 4,4'-dimethylbiphenyl, is used as an additive for an electrolytic solution. It is described that the organic compound such as the above-mentioned anisole derivative or biphenyl derivative generates a redox shuttle in the battery, so that the safety of the battery is assured.

35

- [0007] JP-A-9-106835 (corresponding to United States Patent 5,879,834) describes a measure for assuring safety of a battery under the overcharge condition by increasing an internal resistance in the battery. The increase of an internal resistance can be accomplished using a monomer such as biphenyl, 3-R-thiophene, 3-chlorothiophene or furan in an amount of approx. 1 to 4% to polymerize the compound such as biphenyl at a voltage exceeding the maximum working voltage of the battery.

40

- [0008] JP-A-9-171840 (corresponding to United States Patents 5,776,627 and 6,033,797) also describes a measure for assuring safety of a battery under the overcharge condition, by working an internal current breaker in the battery. The internal current breaker can be worked using a monomer such as biphenyl, 3-R-thiophene, 3-chlorothiophene or furan in an amount of approx. 1 to 4% to polymerize a compound such as biphenyl and produce a gas at a voltage exceeding the maximum working voltage of the battery.

45

- [0009] JP-A-10-321258 also describes a measure for assuring safety of a battery under the overcharge condition, by producing an electroconductive polymer in the battery. The production of an electroconductive polymer can be accomplished by using a monomer such as biphenyl, 3-R-thiophene, 3-chlorothiophene or furan in an amount of approx. 1 to 4% to polymerize the compound at a voltage exceeding the maximum working voltage of the battery.

50

- [0010] JP-A-10-275632 describes that a nonionic aromatic compound having an alkyl group is incorporated into an organic electrolytic solution of a secondary battery which comprises a linear ester as a main solvent. As the nonionic aromatic compound having an alkyl group, there are mentioned a trimellitic ester, tri-2-ethyl trimellitate, dimethyl phthalate, dibutyl phthalate, butylbenzene (normal, tertiary, or iso), cyclohexylbenzene and toluene.

55

- [0011] JP-A-11-16251 (corresponding to United States Patent 6,074,777) describes that the addition of biphenyl or the like is apt to lower the battery performances such as cycle property when the battery is subjected to repeated cyclic procedure in which the battery is charged to a voltage exceeding the maximum voltage of 4.1 V, or the battery is charged and discharged at a high temperature such as 40°C or higher for a long period of time, and that these problems are

more apparently noted when the additive is added in an increased amount. This publication further describes that an electrolytic solution containing 2,2-diphenylpropane or its analogous compound is favorably employed for assuring the safety of a battery under the overcharge condition because 2,2-diphenylpropane or its analogous compound polymerizes to generate a gas, resulting in working of an internal current breaker, or to give an electroconductive polymer, resulting in generation of internal short-circuit.

[0012] The anisole derivatives and biphenyl derivatives described in JP-A-7-302614 and JP-A-2000-156243 favorably work under the condition of overcharge by utilizing redox shuttle, but give adverse effects to the cycle property and storage endurance. In more detail, the anisole derivatives and biphenyl derivatives gradually decompose when the battery is subjected to the repeated charge-discharge procedure, if they are locally subjected to an elevated voltage in the case that the battery is used at a temperature of 40°C or higher, or that the battery is used at an ordinary working voltage. Therefore, the contents of the anisole derivative and biphenyl derivatives decrease by decomposition in the course of actual uses of the battery, so that the desired safety cannot be assured when the charge-discharge procedure is carried out after 300 cycle charge-discharge procedure is repeated.

[0013] Likewise, biphenyl, 3-R-thiophene, 3-chlorothiophene, and furan which are described in JP-A-9-106835, JP-A-9-171840, and JP-A-10-321258 favorably functions under the overcharge condition. However, as indicated in the aforementioned JP-A-11-162512, they give adverse effects to the cycle property and storage endurance. These problems are more prominently noted when the amount of biphenyl increases. In more detail, since biphenyl or the like decomposes by oxidation at a potential of 4.5 V or lower, the content of biphenyl or the like gradually decreases when it is locally subjected to somewhat high voltage in the course of working at 40°C or higher or at an ordinary working voltage, resulting in decrease of the cycle life. Further, since the content of biphenyl or the like decreases due to its decomposition, the desired safety is sometimes not assured when the charge-discharge procedure is carried out after the 300 cycle charge-discharge procedure is repeated.

[0014] In addition, a battery containing 2,2-diphenylpropane and its analogous compound (which is described in JP-A-11-162512) shows only unsatisfactory safety under the overcharge condition, but the attained safety is higher than a battery having no such additive. On the other hand, it is known that the battery containing 2,2-diphenylpropane and its analogous compound shows a cycle property better than a battery containing biphenyl, but worse than a battery containing no additive. Thus, if a battery showing a cycle property better than that attained by the battery containing biphenyl is required, safety should be sacrificed.

[0015] It is an object of the present invention to provide a lithium secondary battery showing high safety under the overcharge condition, and excellent battery performances in cycle property, electric capacity and storage endurance, and further provide a non-aqueous electrolytic solution favorably employable for preparing the lithium secondary battery.

[Disclosure of Invention]

[0016] The invention resides in a non-aqueous electrolytic solution for lithium secondary batteries comprising a non-aqueous solvent and an electrolyte, which further contains 0.1 wt.% to 10 wt.% of a tert-alkylbenzene compound and 0.1 wt.% to 1.5 wt.% of a biphenyl compound.

[0017] The tert-alkylbenzene compound to be incorporated into the non-aqueous electrolytic solution of the invention preferably has a formula of $(R^1)(R^2)(R^3)C-\phi^1$ in which each of R^1 , R^2 , and R^3 independently is an alkyl group of 1 to 4 carbon atoms, and ϕ^1 represents a benzene ring that may have 1 to 5 substituents on the ring. Particularly preferred is a compound having no substituent on the benzene ring. Most preferred tert-alkylbenzene compounds are tert-butylbenzene and tert-pentylbenzene. Moreover, a compound having 1 to 5 hydrocarbyl groups and/or halogen atoms on the benzene ring as the substituents is preferred.

[0018] The biphenyl compound to be incorporated into the non-aqueous electrolytic solution is preferably represented by $\phi^2-\phi^3$ in which each of ϕ^2 and ϕ^3 is a benzene ring that may have 1 to 5 substituents on the ring. Examples of the biphenyl compounds include biphenyl, o-terphenyl, m-terphenyl, p-terphenyl, 4-methylbiphenyl, 4-ethylbiphenyl, and 4-tert-butylbiphenyl. The biphenyl compound to be employed in the invention preferably shows an oxidation potential of 4.5 V or lower.

[0019] Further, the invention resides in a non-aqueous electrolytic solution for lithium secondary batteries comprising a non-aqueous solvent and an electrolyte, which further contains 0.1 wt.% to 20 wt.% of a tert-alkylbenzene compound (in which the tert-alkyl group has 5 to 13 carbon atoms). A representative example of the tert-alkylbenzene compound is tert-pentylbenzene. In other words, the tert-alkylbenzene compound having 5 to 13 carbon atoms can be employed for accomplishing the object of the invention without the biphenyl compound.

[0020] Furthermore, the invention resides in a lithium secondary battery comprising a positive electrode comprising a compound oxide containing lithium and cobalt, nickel or manganese, a negative electrode comprising lithium metal, lithium alloy or material capable of receiving and releasing lithium, and a non-aqueous electrolytic solution of the above-mentioned invention.

[0021] As described hereinbefore, the previously known methods for obviating overcharge are as follows:

a method of conducting a redox shuttle at a voltage of approx. 4.5 V;
 a method of increasing an internal resistance of a battery by polymerizing an additive at a voltage of 4.5 V or lower;
 a method of forming short-circuit by generating a gas to work an internal current breaker; and
 a method of assuring safety of a battery under the overcharge condition by producing a polymer to generate internal short-circuit.

[0022] In contrast, the present invention utilizes a non-aqueous electrolytic solution containing a tert-alkylbenzene compound as an additive. The mechanism of the invention for assuring safety under the overcharge condition is considered as follows: the tert-alkylbenzene compound decomposes by oxidation at a potential of +4.6 V to +5.0 V (relative value to that of lithium), and cobalt or nickel in the positive electrode rapidly dissolves and deposits on the negative electrode to inhibit a reaction of a carbonate in the non-aqueous electrolytic solution with a lithium metal deposited on the negative electrode.

[0023] Further, in the invention, the internal short circuit may be formed in the battery by the deposition of cobalt or nickel, whereby the overcharge inhibitive effect can be attained and the safety of battery can be assured.

[0024] Furthermore, the addition of a small amount (0.1 wt.% to 1.5 wt.%) of a biphenyl compound together with the tert-alkylbenzene compound increases the overcharge inhibitive effect of the tert-alkylbenzene compound. The addition of a small amount of a biphenyl compound surprisingly further improve the battery performances which has not been expected from the previously accepted knowledge.

[0025] Moreover, since the tert-alkylbenzene compound contained in the non-aqueous electrolytic solution has such a high oxidation potential as +4.6 V to +5.0 V (relative value to the oxidation potential of lithium), the tert-alkylbenzene compound does not decompose under a locally occurring high voltage such as higher than 4.2 V in the case that the battery is used at such a high temperature as 40°C or higher, and the charge-discharge procedure is repeated at an ordinary voltage.

[0026] The addition of a small amount (0.1 wt.% to 1.5 wt.-%) of a biphenyl compound alone cannot inhibit overcharge of a battery. It is discovered, however, that it is effective to improve the battery performances, when it is employed in combination with a tert-alkylbenzene compound. This is considered that the decomposition of the biphenyl compound is low. Further, since the tert-alkylbenzene brings about an effect to inhibit overcharge, the safety of a battery is accomplished even in the case that a 300 cycle overcharge test is carried out. Therefore, it is considered that a lithium secondary battery showing not only the safety under the overcharge condition but also high battery performances in the cycle property, electric capacity and storage endurance can be manufactured.

[Detailed Description of Invention]

[0027] Examples of the tert-alkylbenzene compounds to be dissolved in an electrolytic solution comprising a non-aqueous solution and an electrolyte include the following compounds:

tert-butylbenzene, 1-fluoro-4-tert-butylbenzene, 1-chloro-4-tert-butylbenzene, 1-bromo-4-tert-butylbenzene, 1-iodo-4-tert-butylbenzene, 5-tert-butyl-m-xylene, 4-tert-butyltoluene, 3,5-di-tert-butyltoluene, 1,3-di-tert-butylbenzene, 1,4-di-tert-butylbenzene, 1,3,5-tri-tert-butylbenzene, tert-pentylbenzene, (1-ethyl-1-methylpropyl) benzene, (1,1-diethylpropyl)benzene, (1,1-dimethylbutyl)benzene, (1-ethyl-1-methylbutyl) benzene, (1-ethyl-1-ethylbutyl) benzene, (1,1,2-trimethylpropyl)benzene, 1-fluoro-4-tert-pentylbenzene, 1-chloro-4-tert-pentylbenzene, 1-bromo-4-tert-pentylbenzene, 1-iodo-4-tert-pentylbenzene, 5-tert-pentyl-m-xylene, 1-methyl-4-tert-pentylbenzene, 3,5-di-tert-pentyltoluene, 1,3-di-tert-pentylbenzene, 1,4-di-tert-pentylbenzene, and 1,3,5-tri-tert-pentylbenzene.

[0028] The tert-alkylbenzene compounds can be employed singly or in combination of two or more compounds.

[0029] A preferred tert-alkylbenzene compound to be added to the non-aqueous electrolytic solution of the invention is a compound having the formula of (R¹) (R²) (R³)Cφ¹ [in which R¹ is an alkyl group of 2 to 4 carbon atoms, each of R² and R³ independently is an alkyl group of 1 to 4 carbon atoms, and φ¹ represents a benzene ring that may have 1 to 5 substituents on the ring]. The use of this compound is effective to improve particularly the cycle property of the non-aqueous electrolytic solution.

[0030] In the formula of (R¹) (R²) (R³)C-φ¹, R¹ preferably is an alkyl group such as ethyl, propyl or butyl, and each of R² and R³ independently is an alkyl group such as methyl, ethyl, propyl, or butyl. The alkyl group can be a linear or branched alkyl group.

[0031] In the benzene ring that may have 1 to 5 substituents on the ring which is represented by φ¹, each of the substituents preferably is independently a linear alkyl group such as methyl, ethyl, propyl or butyl, or a branched alkyl group such as isopropyl, isobutyl, sec-butyl, tert-butyl, or tert-pentyl. Otherwise, the substituent can be a cycloalkyl group

having 3 to 6 carbon atoms such as cyclopropyl or cyclohexyl; phenyl; benzyl; or an alkylated phenyl or benzyl group such as tolyl, tert-butylphenyl, tert-butylbenzyl, or tert-pentylphenyl; a halogen atom such as fluorine, chlorine, bromine, or iodine. The benzene ring preferably has a hydrocarbonyl group having 1 to 12 carbon atoms or a halogen atom.

[0032] Examples of the above-mentioned tert-alkylbenzene compounds include tert-pentylbenzene, (1-ethyl-1-methylpropyl)benzene, (1,1-diethylpropyl)benzene, (1,1-dimethylbutyl)benzene, (1-ethyl-1-methylbutyl)benzene, (1-ethyl-1-ethylbutyl)benzene, and (1,1,2-trimethylpropyl)benzene. Examples of tert-pentylbenzene derivatives include 1-methyl-4-tert-pentylbenzene, 5-tert-pentyl-m-xylene, 1,3-di-tert-pentylbenzene, 1,4-di-tert-pentylbenzene, 1,3,5-tri-tert-pentylbenzene, 4-bromo-tert-pentylbenzene, 4-fluoro-tert-pentylbenzene, 4-chloro-tert-pentylbenzene, and 4-iodo-tert-pentylbenzene.

[0033] Examples of the biphenyl compounds include biphenyl, o-terphenyl, m-terphenyl, p-terphenyl, 4-methylbiphenyl, 4-ethylbiphenyl, and 4-tert-butylbiphenyl.

[0034] Particularly, if a portion of the tert-butylbenzene or the like having a high oxidation potential of 4.8 to 5.0 V is replaced with a biphenyl compound having a low oxidation potential of 4.5 V (e.g., o-terphenyl), the safety under the overcharge condition is enhanced.

[0035] If a portion of the tert-alkylbenzene compound is replaced with the biphenyl compound, the content of the tert-alkylbenzene preferably is 10 times or lower, more preferably 0.3 to 5 times, particularly preferably 0.5 to 3 times, as much as the content of the biphenyl compound.

[0036] As described hereinbefore, the combination of the tert-alkylbenzene compound and biphenyl compound which have different oxidation potential is effective to improve the security under the overcharge condition and the battery performances.

[0037] If the amount of the tert-alkylbenzene compound is excessive, the electrolytic solution may show a different electroconductivity and the battery performances may lower. If the amount is excessively low, enough safety-improving effect cannot be accomplished. Accordingly, the amount preferably is in the range of 0.1 to 10 wt.%, more preferably 1 to 5 wt.%, based on the amount of the electrolytic solution.

[0038] If the amount of the biphenyl compound is excessive, the biphenyl may decompose in the battery even under ordinary working conditions, and the battery performances may lower. If the amount is excessively low, enough safety-improving effect, and battery performances cannot be accomplished. Accordingly, the amount preferably is in the range of 0.1 to 1.5 wt.%, more preferably in the range of 0.3 to 0.9 wt.%, based on the amount of the electrolytic solution.

[0039] Examples of the non-aqueous solvents employable for the preparation of the non-aqueous electrolytic solution of the invention include cyclic carbonates such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC); lactones such as γ -butyrolactone; linear carbonates such as dimethyl carbonate (DMC), methyl ethyl carbonate (MEC), and diethyl carbonate (DEC); ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, and 1,2-dibutoxyethane; nitriles such as acetonitrile; esters such as methyl propionate, methyl pivalate, and octyl pivalate; and amides such as dimethylformamide.

[0040] The non-aqueous solvents can be employed singly or in combination of two or more solvents. There are no limitations with respect to possible combinations. Examples are combinations of a cyclic carbonate and a linear carbonate, a cyclic carbonate and a lactone, and three cyclic carbonates and a linear carbonate.

[0041] Examples of the electrolytes to be dissolved in the non-aqueous solvent for the preparation of a non-aqueous electrolytic solution include LiPF_6 , LiBF_4 , LiClO_4 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiPF}_4(\text{CF}_3)_2$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$, $\text{LiPF}_3(\text{CF}_3)_3$, $\text{LiPF}_3(\text{iso-C}_3\text{F}_7)_3$, and $\text{LiPF}_5(\text{iso-C}_3\text{F}_7)_2$. These electrolytes can be employed singly or in combination of two or more electrolytes. Generally, the electrolyte can be incorporated into the non-aqueous solvent in such an amount to give an electrolytic solution of 0.1 M to 3 M, preferably 0.5 M to 1.5 M.

[0042] The electrolytic solution can be prepared, for instance, by mixing the above-mentioned non-aqueous solvents; dissolving the electrolyte in the mixture; and further dissolving at least one tert-alkylbenzene compound and optionally at least one biphenyl compound in the mixture solution.

[0043] The electrolytic solution of the invention is favorably employable for manufacture of a secondary battery, particularly lithium secondary battery. There are no limitations with respect to materials of the secondary battery other than the electrolytic solution, and various known materials can be employed.

[0044] The positive electrode active material preferably comprises a compound metal oxide containing lithium and cobalt or nickel. Examples of the compound metal oxides include LiCoO_2 , LiNiO_2 , $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ ($0.01 < x < 1$), and LiMn_2O_4 . Further, an appropriate mixture such as a mixture of LiCoO_2 and LiMn_2O_4 , a mixture of LiCoO_2 and LiNiO_2 , and a mixture of LiMn_2O_4 and LiNiO_2 can be employed.

[0045] The positive electrode can be manufactured by kneading the above-mentioned positive electrode active material, an electro-conductive material such as acetylene black or carbon black, and a binder such as poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVDF), styrene-butadiene copolymer (SBR), acrylonitrilebutadiene copolymer (NBR) or carboxymethylcellulose (CMC) to give a positive electrode composition; coating the positive electrode composition on a collector such as aluminum foil, stainless foil, or lath plate; drying the coated composition; pressing

the dried composition; and heating the pressed composition under vacuum at a temperature of approximately 50 to 2500°C for approximately 2 hours.

[0046] As the negative electrode (negative electrode active material), a lithium metal, a lithium alloy, a carbonaceous material which can absorb and release lithium [e.g., thermally decomposed carbonaceous material, coke, graphites such as artificial graphite and natural graphite, fired organic polymer, and carbon fiber], or a compound tin oxide can be employed. It is preferred to employ a carbonaceous material having a graphite crystal structure in which the lattice distance of lattice surface (002), namely, d_{002} , is in the range of 0.335 to 0.340 nm (nanometer). The negative electrode active material in the powdery form such as carbonaceous powder is preferably used in combination with a binder such as ethylene propylene diene terpolymer (EPDM), polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), styrene-butadiene copolymer (SBR), acrylonitrile-butadiene copolymer (NBR) or carboxymethylcellulose (CMC).

[0047] There are no specific limitations with respect to the structure of the lithium secondary battery of the invention. For instance, the secondary battery can be a battery of coin type comprising a positive electrode, a negative electrode, and a separator in a single or plural layers, or a cylindrical or prismatic battery comprising a positive electrode, a negative electrode, and a separator roll. The separator can be made of microporous film, woven fabric or non-woven fabric.

[0048] The lithium secondary battery of the invention shows good cycle property for a long period of time even if it is used to work at a maximum working voltage of 4.2 V or higher, and the good cycle property can be maintained even if it is used to work at a maximum working voltage of 4.3 V. The cut-off voltage can be set to 2.0 V or higher, and further can be set to 2.5 V or higher. There is no limitation with respect to a current value, but a constant current of 0.1 to 3C is generally utilized. The battery of the invention can be charged and discharged in such a wide temperature range of -40°C to 100°C. However, the temperature preferably is within 0 to 80°C.

[Example 1]

1) Preparation of electrolytic solution

[0049] In a non-aqueous mixture of EC/PC/DEC=30/5/65 (volume ratio) was dissolved LiPF_6 to give an electrolytic solution of 1M concentration. Subsequently, 2.5 wt.% of tert-butylbenzene and 0.9 wt.% of biphenyl were added to the electrolytic solution.

2) Manufacture lithium secondary battery and measurement of its battery performances

[0050] LiCoO_2 (positive electrode active material, 90 wt.%), acetylene black (electro-conductive material, 5 wt.%), and poly(vinylidene fluoride) (binder, 5 wt.%) were mixed. To the resulting mixture further added 1-methyl-2-pyrrolidone, to give a slurry. Thus produced slurry was coated on aluminum foil, dried, and pressed to give a positive electrode.

[0051] Artificial graphite (negative electrode active material, 95 wt. %) and poly (vinylidene fluoride) (binder, 5 wt. %) were mixed. To the resulting mixture was further added 1-methyl-2-pyrrolidone to give a slurry. Thus produced slurry was coated on copper foil, dried, and pressed to give a negative electrode.

[0052] A microporous polypropylene film separator and the above-mentioned electrolytic solution were placed in a cylindrical case to give a cylinder-type battery of 18650 size (diameter: 18 mm, height: 65 mm). To the battery were provided a pressure releasing port and an internal current breaker.

[0053] For performing a cycle test using the 18650 battery, the battery was charged at an elevated temperature (45°C) with a constant electric current of 1.45 A (1C) under a constant voltage to reach 4.2 V for 3 hours in total. Subsequently, the battery was discharged to give a constant electric current 1.45 A (1C) to give a terminal voltage of 2.5 V. The charge-discharge cycle was repeated.

[0054] The initial discharge capacity was almost the same as the capacity measured in a battery using an 1M LiPF_6 and EC/PC/DEC (30/5/65, volume ratio) solvent mixture [Comparison Example 1].

[0055] After a 300 cycle charge-discharge procedure, the retention of discharge capacity was 84.4% of the initial discharge capacity (100%). Further, the battery showed good high temperature storage endurance.

[0056] Subsequently, the 18650 battery having been subjected to the 300 charge-discharge cycle test was excessively charged at a room temperature (20°C) from a fully charged condition using a constant current of 2.9 A (2C), for evaluating a resistance to the overcharging. It was confirmed that the current broke after 22 minutes, and the highest surface temperature of the battery after the breakage of current was 67°C.

[0057] The materials of the tested 18650 size cylinder battery and the battery performances are set forth in Table 1.

[Example 2]

[0058] The procedures of Example 1 were repeated except that the amount of biphenyl in the electrolytic solution

was changed to 0.5 wt.%, to prepare a cylinder battery.

[0059] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Example 3]

[0060] The procedures of Example 1 were repeated except that the amount of biphenyl in the electrolytic solution was changed to 1.3 wt.%, to prepare a cylinder battery.

[0061] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Example 4]

[0062] The procedures of Example 1 were repeated except that the amount of biphenyl in the electrolytic solution was replaced with 0.9 wt.% of o-terphenyl, to prepare a cylinder battery.

[0063] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Example 5]

[0064] The procedures of Example 1 were repeated except that the tert-butylbenzene was replaced with 2.5 wt.% of tert-pentylbenzene and the biphenyl was replaced with 0.9 wt.% of 4-ethylbiphenyl in the electrolytic solution, to prepare a cylinder battery.

[0065] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Example 6]

[0066] The procedures of Example 1 were repeated except that tert-butylbenzene and tert-pentylbenzene were employed as tert-alkylbenzene compounds in an amount of 2 wt.% for each, and 4-methylbiphenyl was employed as the biphenyl compound in an amount of 0.5 wt.% in the electrolytic solution, to prepare a cylinder battery.

[0067] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 1]

[0068] The procedures of Example 1 were repeated except that neither tert-alkylbenzene compound nor biphenyl compound was incorporated, to prepare a cylinder battery.

[0069] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 2]

[0070] The procedures of Example 1 were repeated except that biphenyl was employed in an amount of 1.3 wt.% in the electrolytic solution and no tert-alkylbenzene compound was incorporated, to prepare a cylinder battery.

[0071] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 3]

[0072] The procedures of Comparison Example 2 were repeated except that biphenyl was employed in an amount

of 4 wt.% in the electrolytic solution and no tert-alkylbenzene compound was incorporated, to prepare a cylinder battery.
[0073] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Example 7]

[0074] The procedures of Example 5 were repeated except that LiCoO_2 (positive electrode active material) was replaced with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, to prepare a cylinder battery.

[0075] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 4]

[0076] The procedures of Example 7 were repeated except that neither tert-alkylbenzene compound nor biphenyl compound was incorporated, to prepare a cylinder battery. The battery performances were evaluated.

[0077] The materials of the tested battery and the battery performances are set forth in Table 1.

[Example 8]

[0078] The procedures of Example 1 were repeated except that the tert-butylbenzene was replaced with 4-fluoro-tert-pentylbenzene in an amount of 3.0 wt.% in the electrolytic solution, to prepare a cylinder battery.

[0079] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 5]

[0080] The procedures of Comparison Example 1 were repeated except that 3.0 wt.% of toluene and 0.5 wt.% of biphenyl were employed in the electrolytic solution, to prepare a cylinder battery.

[0081] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 6]

[0082] The procedures of Comparison Example 1 were repeated except that 3.0 wt.% of n-butylbenzene and 0.5 wt.% of biphenyl were employed in the electrolytic solution, to prepare a cylinder battery.

[0083] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 7]

[0084] The procedures of Comparison Example 1 were repeated except that 3.0 wt.% of di-n-butyl phthalate and 0.5 wt.% of biphenyl were employed in the electrolytic solution, to prepare a cylinder battery.

[0085] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

[Comparison Example 8]

[0086] The procedures of Comparison Example 1 were repeated except that 3.0 wt.% of 4-fluorotoluene and 0.5 wt.% of biphenyl were employed in the electrolytic solution, to prepare a cylinder battery.

[0087] The materials of the tested battery, the discharge capacity retention ratio after the 300 cycle charge-discharge procedure, a period of time until breakage of current occurs, and the highest surface temperature of the battery after the breakage of current are shown in Table 1.

Table 1

	Positive electrode Negative electrode	Tert-alkyl-benzene (wt.%) Biphenyl(wt. %)	Electrolytic solution (vol.ratio)	Current breakage High. temperature Discharge capacity retention
5				
10	Ex.1 Graphite	LiCoO ₂ tert-butyl- benzene (2.5) biphenyl (0.9)	1M LiPF ₆ EC/PC/DEC (30/5/65)	22 min. 67°C 84.4%
15	Ex.2 Graphite	LiCoO ₂ tert-butyl- benzene (2.5) biphenyl (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	24 min. 69°C 84.0%
20	Ex.3 Graphite	LiCoO ₂ tert-butyl-benzene (2.5) biphenyl (1.3)	1M LiPF ₆ EC/PC/DEC (30/5/65)	20 min. 66°C 82.7%
25	Ex.4 Graphite	LiCoO ₂ tent-butyl-benzene (2.5) o-terphenyl (0.9)	1M LiPF ₆ EC/PC/DEC (30/5/65)	22 min. 67°C 84.3%
30	Ex.5 Graphite	LiCoO ₂ tert-pentyl-benzene (2.5) 4-ethyl biphenyl (0.9)	1M LiPF ₆ EC/PC/DEC (30/5/65)	21 min. 66°C 82.3%
35	Ex.6 Graphite	LiCoO ₂ tert-butyl-benzene (2) tert-pentyl-benzene (2) 4-methyl-biphenyl (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	21 min. 66°C 85.1%
40				
45	Com. Ex.1 Graphite	LiCoO ₂ None	1M LiPF ₆ EC/PC/DEC (30/5/65)	31 min. thermal runaway 82.8%
	Com. Ex.2 Graphite	LiCoO ₂ biphenyl (1.3)	1M LiPF ₆ EC/PC/DEC (30/5/65)	31 min. thermal runaway 78.3%
50	Com. Ex.3 Graphite	LiCoO ₂ biphenyl (4)	1M LiPF ₆ EC/PC/DEC (30/5/65)	18 min. 83°C 72.1%
55	Ex.7 CO _{0.2} O ₂ Graphite	LiNi _{0.8} tert-pentyl-benzene (2.5) 4-ethyl biphenyl (0.9)	1M LiPF ₆ EC/PC/DEC (30/5/65)	21 min. 67°C 82.5%

Table 1 (continued)

	Positive electrode Negative electrode	Tert-alkyl-benzene (wt.%) Biphenyl(wt. %)	Electrolytic solution (vol.ratio)	Current breakage High. temperature Discharge capacity retention
Com. Ex.4	LiNi _{0.8} CO _{0.2} O ₂ Graphite	None	1M LiPF ₆ EC/PC/DEC (30/5/65)	31 min. thermal runaway 80.4%
Ex.8	LiCoO ₂ Graphite	4-fluoro-tert- pentylbenzene (3) biphenyl (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	23 min. 68°C 84.3%
Com. Ex.5	LiCoO ₂ Graphite	toluene (3) biphenyl (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	31 min. thermal runaway 81.2%
Com. Ex.6	LiCoO ₂ Graphite	n-butyl-benzene (3) biphenyl (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	31 min. thermal runaway 80.1%
Com. Ex.7	LiCoO ₂ Graphite	di-n-butyl-phthalate (3) biphenyl (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	31 min. thermal runaway 78.4%
Com. Ex.8	LiCoO ₂ Graphite	4-fluoro-toluene (3) biphenyl (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	25 min. thermal runaway 79.8%
Remarks: Current breakage: period of time to break current High. temperature: Highest temperature of battery Discharge capacity retention: ratio of discharge capacity after 300 cycle Graphite: Artificial graphite				

[0088] In Examples 1 to 8, a sufficient amount of cobalt or nickel deposited on the negative electrode under the overcharge condition. It is clear that a lithium secondary battery utilizing a non-aqueous electrolytic solution which contains a tert-alkylbenzene compound and a biphenyl compound according to the invention shows safety under the overcharge condition and the cycle property better than the secondary batteries of Comparison Examples.

[Example 11]

1) Preparation of electrolytic solution

[0089] In a non-aqueous mixture of EC/PC/DEC=30/5/65 (volume ratio) was dissolved LiPF₆ to give an electrolytic solution of 1M concentration. Subsequently, 2.0 wt.% of tert-pentylbenzene was added to the electrolytic solution.

2) Manufacture lithium secondary battery and measurement of its battery performances

[0090] LiCoO₂ (positive electrode active material, 80 wt.%), acetylene black (electro-conductive material, 10 wt.%), and poly(vinylidene fluoride) (binder, 10 wt.%) were mixed. To the resulting mixture further added 1-methyl-2-pyrrolidone, to give a slurry. Thus produced slurry was coated on aluminum foil, dried, and pressed to give a positive electrode.

[0091] Artificial graphite (negative electrode active material, 90 art.%) and poly (vinylidene fluoride) (binder, 10 wt. %) were mixed. To the resulting mixture was further added 1-methyl-2-pyrrolidone to give a slurry. Thus produced slurry was coated on copper foil, dried and pressed to give a negative electrode.

[0092] A microporous polypropylene film separator and the above-mentioned electrolytic solution were placed in a coin case to give a coin-type battery (diameter: 20 mm, thickness: 3.2 mm).

[0093] The coin battery was charged at a room temperature (20°C) with a constant electric current of 0.8 mA under a constant voltage to reach 4.2 V for 5 hours. Subsequently, the battery was discharged to give a constant electric current 0.8 mA to give a terminal voltage of 2.7 v. The charge-discharge cycle was repeated.

[0094] The initial discharge capacity was almost the same as the capacity measured in a battery using an 1M LiPF₆ and EC/PC/DEC (30/5/65, volume ratio) solvent mixture containing no tert-alkylbenzene compound [Comparison Example 1].

[0095] After a 50 cycle charge-discharge procedure, the retention of discharge capacity was 92.8% of the initial discharge capacity (100%) . Further, the battery showed good low temperature storage endurance.

[0096] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 12]

[0097] The procedures of Example 11 were repeated except that the amount of tert-pentylbenzene in the non-aqueous electrolytic solution was changed to 5.0 wt.%, to prepare a coin battery.

[0098] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 91.5%.

[0099] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 13]

[0100] The procedures of Example 11 were repeated except that the amount of tert-pentylbenzene in the non-aqueous electrolytic solution was changed to 0.5 wt.%, to prepare a coin battery.

[0101] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 90.3%.

[0102] The materials of the coin battery and the battery performances are set forth in Table 2.

[Comparison Example 11]

[0103] In a non-aqueous mixture of EC/PC/DEC=30/5/65 (volume ratio) was dissolved LiPF₆ to give a non-aqueous electrolytic solution of 1M concentration. In this procedure, no tert-alkylbenzene compound was added.

[0104] A coin battery was manufactured in the same manner as in Example 11, except for employing the above-obtained non-aqueous electrolytic solution, and subjected to the evaluation of battery performances.

[0105] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 82.6%.

[0106] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 14]

[0107] In a non-aqueous mixture of EC/PC/DEC=30/5/65 (volume ratio) was dissolved LiPF₆ to give a non-aqueous electrolytic solution of 1M concentration. Subsequently, 2.0 wt.% of tert-pentyltoluene was added to the non-aqueous electrolytic solution.

[0108] A coin battery was manufactured in the same manner as in Example 11, except for employing the above-obtained non-aqueous electrolytic solution, and subjected to the evaluation of battery performances.

[0109] The initial discharge capacity was almost the same as the capacity measured in a battery using an 1M LiPF₆ and EC/PC/DEC (30/5/65, volume ratio) solvent mixture containing no tert-alkylbenzene compound [Comparison Example 11].

[0110] After a 50 cycle charge-discharge procedure, the retention of discharge capacity was 92.1% of the initial discharge capacity (100%). Further, the battery showed good low temperature storage endurance.

[0111] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 15]

[0112] The procedures of Example 11 were repeated except that (1,1-diethylpropyl)benzene was incorporated in an amount of 2.0 wt.% into the non-aqueous electrolytic solution, to prepare a coin battery.

[0113] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 91.9%.

[0114] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 16]

[0115] The procedures of Example 11 were repeated except that a non-aqueous solvent of EC/PC/DEC/DMC (30/5/30/35, volume ratio) was employed and the artificial graphite was replaced with natural graphite, to prepare a non-aqueous electrolytic solution and manufacture a coin battery.

[0116] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 92.8%.

[0117] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 17]

[0118] The procedures of Example 11 were repeated except that a non-aqueous electrolytic solution of 1M LiPF_6 in EC/PC/MEC/DMC (30/5/50/15, volume ratio) was employed and the LiCoO_2 (positive electrode active material) was replaced with $\text{LiNi}_{0.8}\text{CO}_{0.2}\text{O}_2$, to manufacture a coin battery.

[0119] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 91.1%.

[0120] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 18]

[0121] The procedures of Example 11 were repeated except that a non-aqueous electrolytic solution of 1M LiBF_4 in EC/PC/DEC/DMC (30/5/30/35, volume ratio) was employed and the LiCoO_2 (positive electrode active material) was replaced with LiMn_2O_4 , to manufacture a coin battery.

[0122] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 92.6%.

[0123] The materials of the coin battery and the battery performances are set forth in Table 2.

[Example 19]

[0124] The procedures of Example 11 were repeated except that 4-fluoro-tert-pentylbenzene was employed as the additive in an amount of 3.0 wt.% to the non-aqueous electrolytic solution, to manufacture a coin battery.

[0125] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 92.7%.

[0126] The materials of the coin battery and the battery performances are set forth in Table 2.

[Comparison Example 12]

[0127] The procedures of Example 11 were repeated except that toluene was employed as the additive in an amount of 3.0 wt.% in the non-aqueous electrolytic solution, to manufacture a coin battery.

[0128] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 81.3%.

[0129] The materials of the coin battery and the battery performances are set forth in Table 2.

[Comparison Example 13]

[0130] The procedures of Comparison Example 11 were repeated except that n-butylbenzene was employed as the additive in an amount of 3.0 wt.% in the non-aqueous electrolytic solution, to manufacture a coin battery.

[0131] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 79.7%.

[0132] The materials of the coin battery and the battery performances are set forth in Table 2.

[Comparison Example 14]

[0133] The procedures of Comparison Example 11 were repeated except that di-n-butyl phthalate was employed as the additive in an amount of 3.0 wt.% in the non-aqueous electrolytic solution, to manufacture a coin battery.

[0134] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 78.1%.

[0135] The materials of the coin battery and the battery performances are set forth in Table 2.

[Comparison Example 15]

[0136] The procedures of Comparison Example 11 were repeated except that 4-fluorotoluene was employed as the additive in an amount of 3.0 wt.% in the non-aqueous electrolytic solution, to manufacture a coin battery.

[0137] After the 50 cycle charge-discharge procedure, the retention of discharge capacity was 80.6%.

[0138] The materials of the coin battery and the battery performances are set forth in Table 2.

Table 2

	Positive electrode Negative electrode	Compound (wt.%)	Electrolytic solution (vol.ratio)	Initial discharge capacity (r.v.) Discharge capacity retention
Ex.11	LiCoO ₂ Artificial graphite	tert-pentyl-benzene (2.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	1.03 92.8%
Ex.12	LiCoO ₂ Artificial graphite	tert-pentyl-benzene (5.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	1.02 91.5%
Ex.13	LiCoO ₂ Artificial graphite	tert-pentyl-benzene (0.5)	1M LiPF ₆ EC/PC/DEC (30/5/65)	1.01 90.3%
Com. Ex. 11	LiCoO ₂ Artificial graphite	None	1M LiPF ₆ EC/PC/DEC (30/5/65)	1.00 82.6%
Ex.14	LiCoO ₂ Artificial graphite	1-methyl-4-tert- pentyl-benzene(2.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	1.02 92.1%
Ex.15	LiCoO ₂ Artificial graphite	(1,1-diethyl-propyl)- benzene(2.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	1.02 91.9%
Ex.16	LiCoO ₂ Natural graphite	tert-pentyl-benzene (2.0)	1M LiPF ₆ EC/PC/DEC/DMC (30/5/30/35)	1.02 92.8%
Ex.17	LiNi _{0.8} CO _{0.2} O ₂ Artificial graphite	tert-pentyl-benzene (2.0)	1M LiPF ₆ EC/PC/MEC/DMC (30/5/50/15)	1.15 91.1%
Ex.18	LiMn ₂ O ₄ Artificial graphite	tert-pentyl-benzene (2.0)	1M LiBF ₄ EC/PC/DEC/DMC (30/5/30/35)	0.99 92.6%
Ex.19	LiCoO ₂ Artificial graphite	4-fluoro-tert-pentyl- benzene(3.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	1.02 92.7%

Table 2 (continued)

	Positive electrode Negative electrode	Compound (wt.%)	Electrolytic solution (vol.ratio)	Initial discharge capacity (r.v.) Discharge capacity retention
Com. Ex. 12	LiCoO ₂ Artificial graphite	toluene (3.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	0.98 81.3%
Com. Ex. 13	LiCoO ₂ Artificial graphite	n-butyl-benzene (3.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	0.97 79.7%
Com. Ex. 14	LiCoO ₂ Artificial graphite	di-n-butylphthalate (3.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	0.97 78.1%
Com. Ex. 15	LiCoO ₂ Artificial graphite	4-fluoro-toluene (3.0)	1M LiPF ₆ EC/PC/DEC (30/5/65)	0.98 80.6%

[Utilization in Industry]

[0139] The present invention provides a lithium secondary battery showing high safety under overcharge condition, and excellent battery characteristics in cycle property, electric capacity and storage endurance.

Claims

1. A non-aqueous electrolytic solution for lithium secondary batteries comprising a non-aqueous solvent and an electrolyte, which further contains 0.1 wt.% to 10 wt.% of a tert-alkylbenzene compound and 0.1 wt.% to 1.5 wt.% of a biphenyl compound.
2. The electrolytic solution of claim 1, wherein the tert-alkylbenzene compound is represented by the formula of (R¹) (R²) (R³)C-φ¹ in which each of R¹, R², and R³ independently is an alkyl group of 1 to 4 carbon atoms, and φ¹ represents a benzene ring that may have 1 to 5 substituents on the ring.
3. The electrolytic solution of claim 2, wherein the tert-alkylbenzene compound has no substituent on the benzene ring.
4. The electrolytic solution of claim 2, wherein the tert-alkylbenzene compound is tert-butylbenzene.
5. The electrolytic solution of claim 2, wherein the tert-alkylbenzene compound is tert-pentylbenzene.
6. The electrolytic solution of claim 2, wherein the tert-alkylbenzene compound has 1 to 5 hydrocarbonyl groups and/or halogen atoms on the benzene ring as the substituents.
7. The electrolytic solution of claim 1, wherein the biphenyl compound is represented by φ²-φ³ in which each of φ² and φ³ independently represents a benzene ring that may have 1 to 5 substituents on the ring.
8. The electrolytic solution of claim 7, wherein the biphenyl compound is selected from the group consisting of biphenyl, o-terphenyl, m-terphenyl, p-terphenyl, 4-methylbiphenyl, 4-ethylbiphenyl, and 4-tert-butylbiphenyl.
9. The electrolytic solution of claim 1, wherein the biphenyl compound shows an oxidation potential of 4.5 V or lower.

10. The electrolytic solution of claim 1, wherein the non-aqueous solvent is at least one compound selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, γ -butyrolactone, dimethyl carbonate, methyl ethyl carbonate, diethyl carbonate, tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-dibutoxyethane, acetonitrile, methyl propionate, methyl pivalate, octyl pivalate and dimethylformamide.
11. A non-aqueous electrolytic solution for lithium secondary batteries comprising a non-aqueous solvent and an electrolyte, which further contains 0.1 wt.% to 20 wt.% of a tert-alkylbenzene compound under the condition that the tert-alkyl group has 5 to 13 carbon atoms.
12. The electrolytic solution of claim 11, wherein the tert-alkylbenzene compound is tert-pentylbenzene.
13. The electrolytic solution of claim 11, wherein the non-aqueous solvent is at least one compound selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, γ -butyrolactone, dimethyl carbonate, methyl ethyl carbonate, diethyl carbonate, tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-dibutoxyethane, acetonitrile, methyl propionate, methyl pivalate, octyl pivalate and dimethylformamide.
14. A lithium secondary battery comprising a positive electrode comprising a compound oxide containing lithium and cobalt, nickel or manganese, a negative electrode comprising lithium metal, lithium alloy, or material capable of receiving and releasing lithium, and a non-aqueous electrolytic solution of claim 1.
15. A lithium secondary battery comprising a positive electrode comprising a compound oxide containing lithium and cobalt, nickel or manganese, a negative electrode comprising lithium metal, lithium alloy, or material capable of receiving and releasing lithium, and a non-aqueous electrolytic solution of claim 11.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/00518

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ H01M 10/40		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ H01M 10/40		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 10-275632 A (Hitachi Maxell, Ltd.), 13 October, 1998 (13.10.1998), Par. No. 0012, etc. (Family: none)	1-15
A	JP 5-36439 A (Sony Corporation), 12 February, 1993 (12.02.1993), Claim 1, etc. (Family: none)	1-15
P,A	JP 2001-167791 A (Ube Industries, Ltd.), 22 June, 2001 (22.06.2001), Claims 1, 2 (Family: none)	1-15
A	JP 2000-058116 A (Sanyo Electric Co., Ltd.), 25 February, 2000 (25.02.2000), Claims 1 to 4, etc. (Family: none)	1-15
P,A	JP 2001-357876 A (Nippon Steel Chemical Co., Ltd.), 26 December, 2001 (26.12.2001), Claim 2, etc. (Family: none)	1-15
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 12 February, 2002 (12.02.02)		Date of mailing of the international search report 26 February, 2002 (26.02.02)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/00518

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0776058 A2 (MOLI ENERGY LIMITED), 28 May, 1997 (28.05.1997), Claim 34 & JP 9-171840 A	1-15
A	EP 0759641 A1 (MOLI ENERGY LIMITED), 26 February, 1997 (26.02.1997), Claims 1-26 & JP 9-106835 A)	1-15
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